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(54) ANTIBACTERIAL PRECOATED METAL SHEET

(57)Abstract:

PURPOSE: To produce an antibacterial precoated metal sheet which is excellent in antibacterial properties and in the processibility after baking, does not exhibit the discoloration of a coating film for a long term, and long retains antibacterial properties.

CONSTITUTION: This metal sheet has at least two baked coating layers the outermost layer of which is a baked clear layer contg. 0.1-5wt.% (in term of solid) antibacterial agent comprising a silver-ion-carrying zeolite carrier having a particle size of 0.05-5 $\mu$ m.

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CLAIMS

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[Claim(s)]

[Claim 1] The antibacterial precoat metal plate which has a coat more than two-layer, is an antibacterial precoat metal plate whose best layer is a clear layer, and is characterized by containing the antimicrobial agent which consists of a zeolite system support with a particle size of 0.05-5 micrometers which made the complex ion support in the baking coat of the aforementioned clear layer 0.1 to 5% of the weight on solid-content criteria.

[Claim 2] The antibacterial precoat metal plate which has a coat more than two-layer, is an antibacterial precoat metal plate whose best layer is a clear layer, and is characterized by containing the antimicrobial agent which consists of a zeolite system support with a particle size of 0.05-5 micrometers which made the complex ion of 40 % of the weight or more, and 60 or less % of the weight of at least one sort of metal ions of copper, zinc, and a lithium support in the baking coat of the aforementioned clear layer 0.1 to 5% of the weight on solid-content criteria.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] Especially this invention is excellent in antibacterial and the processability after baking finish, and about an antibacterial precoat metal plate, even if it uses it for a long period of time, it does not have discoloration of a paint film, and it relates to the antibacterial precoat metal plate with which antibacterial is maintained.

[0002]

[Description of the Prior Art] Since building materials, such as household-electric-appliances articles, such as a refrigerator and a washing machine, a bathroom, a kitchen, a roof, a sliding shutter, and a shutter, the duct for air conditionings, etc. are used under the environment where moisture is contacted frequently, a bacillus tends to adhere. If a bacillus carries out accretion to a front face, it is not only insanitary, but the problem that it is conspicuous as dirt will arise. Therefore, paint of the metal plate used for the above-mentioned use is expected antibacterial.

[0003] Applying an antibacterial covering constituent to various building materials, such as a wood slab and a panel, concrete, mortar, etc. by the spray method, the air sol method, brush coating, etc., and carrying out ordinary temperature dryness for such a purpose, is proposed (for example, JP, 4-214772, A, JP, 5-98475, A, etc.). However, when alcohol etc. is used in order to remove the bacillus on the front face of a paint film since it is inferior to chemical resistance in the case of an air drying paint film, paint may dissolve. Moreover, since it must paint to each coated object in the case of such a post coat method, there is also a problem of being inferior to productivity. Then, it is desirable to consider as the painted so-called "precoat" metal plate carried out before carrying out a fabricating operation to a complicated configuration, while giving good chemical resistance.

[0004] Therefore, the purpose of this invention is offering the antibacterial precoat metal plate with which it excels in antibacterial and the processability after baking finish, and there is no discoloration of a paint film even if it uses it for a long period of time, and antibacterial is maintained.

[0005]

[Means for Solving the Problem] Even if it excels in antibacterial and the processability after baking finish by making a specific antimicrobial agent contain in the baking coat of a clear layer in the antibacterial precoat metal plate which is the clear layer of the best layer by this invention persons having a coat more than two-layer as a result of wholeheartedly research and uses it in view of the above-mentioned purpose for a long period of time, there is no discoloration of a paint film, and it found out that the antibacterial precoat metal plate with which antibacterial is maintained was obtained, and hit on an idea to this invention.

[0006] That is, the antibacterial precoat metal plate of this invention has a coat more than two-layer, is an antibacterial precoat metal plate whose best layer is a clear layer, and is characterized by containing the antimicrobial agent which consists of a zeolite system support with a particle size of 0.05-5 micrometers which made the complex ion support in the baking coat of the aforementioned clear layer 0.1 to 5% of the weight on solid-content criteria.

[0007] this invention is explained to a detail below.

[1] Clear layer (1) The antimicrobial agent used for an antimicrobial agent this invention makes a zeolite system support support at least one sort of metal ions of copper, zinc, and a lithium further by using as an indispensable component the complex-ion independent which has an antibacterial action, or a complex ion. When making two or more sorts of metal ions support, the rate of a complex ion is 40 % of the weight or more, and the rate of the ion of at least one sort of metals of copper, zinc, and a lithium is 60 or less % of the weight.

[0008] Specific surface area of a zeolite is large, ion exchange capacity is more than 3 meq/g (anhydrous criteria), and its thing with the large ion-exchange speed is desirable. As such a zeolite, in permutite, A type, an X type or Y type zeolite, a synthetic mordenite, etc. are mentioned, and, on the other hand, a mordenite, a clo knob tytolite, a CHABA site, etc. are mentioned by the natural zeolite.

[0009] By [ which have such a property ] carrying out zeolite use, the amount of maintenance independent [ an antibacterial metal ion ] or multiple can be arbitrarily adjusted by the ion-exchange method, and the antimicrobial agent

which has antibacterial [ desired ] can be prepared. Thus, by making a zeolite support an antibacterial metal ion, a metal ion can prevent that a paint film discolors in response to the time of carrying out baking finish with a paint component.

[0010] As for the rate of the antibacterial metal ion to a zeolite system support, it is desirable that it is 0.5 - 10 % of the weight, and it is more desirable that it is 0.5 - 5 % of the weight. If the rate of antibacterial of an antibacterial metal ion is low at less than 0.5 % of the weight and 10 % of the weight is exceeded on the other hand, the storage stability of a paint will fall.

[0011] With various dispersers, a grinder, etc., preferably, particle size carries out pulverization of the 0.05-5 micrometers of such antimicrobial agents so that it may be set to 0.05-3 micrometers. When particle size is less than 0.05 micrometers, for a low reason, the rate which a part of antimicrobial agent particle exposes to a paint film front face is not acquired for antibacterial [ sufficient ]. On the other hand, if 5 micrometers is exceeded, since the specific surface area of an antimicrobial agent becomes small, antibacterial will fall, and the storage stability and the workability of a paint will get worse.

[0012] The addition of the antimicrobial agent used for this invention is 0.5 - 2 % of the weight preferably 0.1 to 5% of the weight as a solid content in a hardening paint film. The addition of antibacterial of an antimicrobial agent is low at less than 0.1 % of the weight. If 5 % of the weight is exceeded, while the storage stability of a paint will become bad on the other hand, the rate of discoloration of a paint film becomes high.

[0013] (2) If the paint film formation resin used for the paint which mixes the paint above-mentioned antimicrobial agent is a burned type, anything of a type can be used, for example, acrylic resin, silicone denaturation acrylic resin, polyester resin, silicone denaturation polyester resin, a fluororesin, etc. will be mentioned.

[0014] The resin which carried out the polymerization by the usual method as acrylic resin from monomers, such as ethylene nature monomers, such as acrylic-acid (meta) alkyl ester, such as ethylene nature monomers, such as an ethylene nature monomer which has hydroxyls, such as acrylic-acid (meta) hydroxymethyl and acrylic-acid (meta) hydroxy butyl, an acrylic acid (meta), and a crotonic acid, a methyl acrylate (meta), and an acrylic-acid (meta) propyl, and styrene, is mentioned. Moreover, to the above-mentioned acrylic resin 100 weight section, silicone denaturation acrylic resin can make organic silicone (for example, organic silicone of number average molecular weight 300-1000 which has -SiOCH<sub>3</sub> and -SiOH as a functional group) 5 - 50 weight sections able to react, and can be obtained.

[0015] As polyester resin, the resin which used one sort or the polyhydric alcohol beyond it, such as ethylene glycol, a polyethylene glycol, butanediol, and hydrogenation bisphenol A, and base acids, such as a phthalic acid, a tetrahydrophthalic acid, a maleic acid, a succinic acid, and cyclohexane-1,4-dicarboxylic acid, as the raw material is mentioned. Moreover, to the above-mentioned polyester resin 100 weight section, silicone denaturation polyester resin can make above-mentioned organic silicone 5 - 50 weight sections able to react, and can be obtained. If needed, fats and oils or a fatty acid can be added to such polyester resin to about 30 % of the weight, and flexibility can be given to it.

[0016] Moreover, as a fluororesin, hardened type fluorine paints, such as a fluoro olefin vinyl ether copolymer besides being polyvinylidene fluoride resin, a polyvinyl fluoride, etc. and a fluoro olefin vinyl-ester copolymer, can be used.

[0017] To the above-mentioned paint film formation resin, you may add a curing agent if needed. As a curing agent, amino resin, such as melamine resin, a guanamine resin, and a urea-resin, a block isocyanate, etc. are mentioned. Moreover, an organic pigment, colors, etc., such as inorganic pigments, such as titanium oxide, carbon black, and a Synthetic Ochre, and a copper phthalocyanine blue, a Phthalocyanine Green, Quinacridone red, can be added if needed.

[0018] (3) The thickness of the clear layer containing a thickness antimicrobial agent has desirable 1-5 micrometers, and its 2-5 micrometers are more desirable. When the thickness of a clear layer is less than 1 micrometer, a paint film tends to exfoliate by the fabricating operation after paint. If 5 micrometers is exceeded, since the rate which an antimicrobial agent exposes from a paint film front face will fall on the other hand, antibacterial [ sufficient ] is not obtained.

[0019] [2] As a lower layer of the above-mentioned clear layer which carries out antimicrobial agent content, the antibacterial precoat metal plate of a lower layer this invention has a chemical-conversion layer, an under coat, and finishing coat, and may prepare a middle-coat layer if needed. A pigment or a color may color an under coat, a middle-coat layer, and finishing coat. In addition, the thickness of an under coat has desirable 3-7 micrometers, and the thickness of finishing coat has desirable 5-40 micrometers. Moreover, when there is a middle-coat layer, the thickness has desirable 5-15 micrometers.

[0020] [3] Form the clear layer of the antibacterial precoat metal plate of this invention after performing degreasing processing and a chemical conversion to the paint film formation method metal plate by the well-known method and carrying out middle-coat paint to it under coat paint, finishing paint, and if needed. Especially the method of application is not limited but can use the usual methods of application, such as air-spray paint an airless spray,

electrostatic coating, roll coat paint, curtain coat paint, and knockout paint.

[0021] As for paint film dryness of the usual precoat metal plate, it is desirable to print for 15 - 150 seconds at 150-300 degrees C. At less than 150 degrees C, a paint film does not fully harden [ baking temperature ], but the antimicrobial agent in a paint film is eluted in the top where the corrosion resistance of a paint film is low, and it may be unable to maintain antibacterial for a long period of time. On the other hand, above 300 degrees C, while a paint film will be in the state of exaggerated BEKU, a paint film yellows or adhesion falls, the function of an antimicrobial agent may fall. In addition, baking of a middle-coat layer and baking of a clear layer which are prepared an under coat, finishing coat, and if needed may be performed simultaneously, and you may carry out one by one. That is, the antibacterial precoat metal plate of this invention can be formed by the two quart 1 BEKU method, the two quart 2 BEKU method, the three quart 3 BEKU method, the four quart 4 BEKU method, etc.

[0022] Thus, in order to remove a bacillus, even if it wipes with alcohol etc. the antibacterial precoat metal plate of this invention obtained by printing the paint containing an antimicrobial agent and drying, a paint film dissolves, or it does not deteriorate and can maintain antibacterial for a long period of time. Moreover, since the antibacterial precoat metal plate of this invention contains an antimicrobial agent only in a clear layer, the addition of an antimicrobial agent can press it down few.

[0023]

[Example] Although the following examples and examples of comparison explain this invention in detail, this invention is not limited to them.

Examples 1-3 and examples 1-4 of comparison (1) Zn: Hot-dip zinc-coated carbon steel sheet (2) aluminum: Aluminum plating steel plate (3) Zn/aluminum: Zinc-aluminum alloy plating steel plate (aluminum 5%)

[0024] 2. The chemical conversion was performed by the well-known method to each metal plate of the chemical-conversion above. In addition, at an example 1 and the examples 3 and 4 of comparison, it is 0.8g (the surfboard dyne ZS9200, Nippon Paint Co., Ltd. make) of processing liquid of a phosphoric-acid zinc system/, and m2. It applied. Moreover, in the example 2, processing liquid (ARUSAFU 401/45, Nippon Paint Co., Ltd. make) 20 mg/m2 (the amount criteria of chromium) of a clo mate system was applied, and processing liquid (made in [ Nippon Paint Co., Ltd. ] surfboard coat NRC 300) 20 mg/m2 (the amount criteria of chromium) of a clo mate system was applied in other examples.

[0025] 3. The under coat was performed using the paint shown in the under coat table 1. In examples 1-3 and the examples 2-4 of comparison, the under coat was performed by the roll-coater method, and it burned in the baking temperature (attainment board temperature) and time which are shown in Tables 2 and 4. The dryness thickness of the obtained paint film is as being shown in Tables 2 and 4. Moreover, as shown in Table 3, at the example 1 of comparison, it is kg [ acrylic emulsion type / [paint 4 and Nippon Paint Co., Ltd. make] made from BINIREKKUSU 60 (white) 0.13]/m2 by the roller method. It applied and dried in ordinary temperature.

[0026] 4. It finished using the paint shown in the finishing table 1. In examples 1-3 and the examples 2-4 of comparison, it finished by the roll-coater method and burned in the baking temperature (attainment board temperature) and time which are shown in Tables 2 and 4. The dryness thickness of the obtained paint film is as being shown in Tables 2 and 4. Moreover, the antimicrobial agent (Ag-Zeolite) which made the zeolite system support of the addition shown in Table 3 at BINIREKKUSU 60 (paint 4) of the acrylic emulsion type used for the under coat support a complex ion with the example 1 of comparison is blended, and a coverage is 0.13 kg/m2. It applied by the roller method so that it might become, and it dried in ordinary temperature.

[0027] 5. In the clear paint examples 1-3 and the examples 2-4 of comparison, using the paint which blended the antimicrobial agent of the kind shown in Tables 2 and 4, and an addition with the clear paint shown in Table 1, clear paint was performed by the roll-coater method, and baking for 20 seconds was performed at the temperature shown in Tables 2 and 4. The dryness thickness of the obtained paint film is as being shown in Tables 2 and 4.

[0028]

Table 1 Sign Tradename P-1 Primer for the flexible coats 150 P-2 Super rack D1F Primer for H-10 (\*\*)

P-3 Primer for uni-chlorofluorocarbon C Paint 1 Flexible coat 150 (white)

paint 2 Super rack D1F J-15 (Brown -- clear)

Paint 3 Uni-chlorofluorocarbon C (white)

Paint 4 BINIREKKUSU 60 (an acrylic emulsion type, white)

C-1 Flexible coat 150 (clear)

C-2 NIPPE super coat 200HQ C-3 Uni-chlorofluorocarbon C (clear)

notes -- all -- the Nippon Paint Co., Ltd. make [0029]

Two table No. Example 1 Example 2 Example 3. A metal plate Zn aluminum Zn/aluminum Board thickness (mm) 0.5 0.5 0.5 A chemical conversion The kind of processing liquid Phosphoric-acid zinc Clo mate Clo mate Under coat The kind of paint P-1P-2P-3 Dryness thickness (micromet r) 77 76 Baking temperature (degree C) 210 210 210 Baking time

(second) 20 20 60 Finishing Kind of paint Paint 1 Paint 2 Paint 3 Dryness thickness (micrometer) 15 15 15 baking temperature (degree C) 210 210 245 baking time (second) 20 20 60 Clear Antimicrobial agent kind (% of the weight) Ag-Zeolite . 100 80 60 Cu-Zeolite - 20 - Zn-Zeolite - - 40 Particle size (micrometer) 0.05 0.5 4 A metal ion/support (1) 0.55 Ten additions (% of the weight) 5 0.1 5 The kind of paint C-1 C-2 C-3 dryness thickness (micrometer) 2 55 Baking temperature (degree C) 190 210 230 Note (1) the antibacterial metal ion to a zeolite system support -- comparatively (% of the weight) --  
[0030]

表 3

例No.	比較例 1
金属板	Al
板厚 (mm)	0.5
化成処理	
処理液の種類	クロメート
下塗り	
塗料の種類	塗料4
塗布量 (kg/m <sup>2</sup> )	0.13
乾燥温度 (°C)	常温
上塗り	
抗菌剤	
種類	Ag-Zeolite
粒径 (μm)	0.1
金属イオン/担持体 <sup>(1)</sup>	3
添加量 (重量%)	8
塗料の種類	塗料4
塗布量 (kg/m <sup>2</sup> )	0.13
乾燥温度 (°C)	常温
クリアー	なし

Note (1) The rate of the antibacterial metal ion to a zeolite system support (% of the weight)

[0031]

Four table No. Example 2 of comparison Example 3 of comparison Example 4 of comparison. A metal plate Zn/aluminum Zn/aluminum Zn/aluminum Board thickness (mm) 0.5 0.5 0.5 A chemical conversion The kind of processing liquid A clo mate Phosphoric-acid zinc Phosphoric-acid zinc Under coat The kind of paint P-1P-1 P-1 Dryness thickness (micrometer) 7 7 7 Baking temperature (degree C) 210 210 210 baking time 20 (second) 20 20 Finishing Kind of paint Paint 1 Paint 1 Paint 1 Dryness thickness (micrometer) 15 15 15 baking temperature (degree C) 210 210 210 Baking time (second) 20 20 20 Clear Antimicrobial agent kind Ag-Zeolite Ag-Zeolite Ag-Zeolite particle size (micrometer) 0.1 8 5 A metal ion/support (1) 3 3 12 Addition (% of the weight) 8 2 5 kind of paint C-1C-1 C-1 dryness thickness (micrometer) 3 4 5 Baking temperature (degree C) 190 210 230 Note (1) the antibacterial metal ion to a zeolite system support -- comparatively (% of the weight) --

[0032] 6. physical-properties evaluation of a physical-properties evaluation on profit \*\*\*\* ant bact rial precoat met l plat -- the following -- it went to pass These results are shown in Table 5.

[0033] (1) cut the antibacterial profit \*\*\*\* antibacterial precoat metal plate, produced the 60mmx50mm test piece, the methicillin-resistant staphylococcus aureus (MRSA) was made to adhere to this test piece, and the number of micro organisms after 24-hour progress (a cell/ml) was investigated Moreover, in order to investigate a self-sustaining antibacterial one, MRSA was made to adhere like the test piece one year after paint, and the number of micro organisms after 24-hour progress (a cell/ml) was investigated. In order to investigate antibacterial [ after washing ] furthermore, after washing the test piece one year after paint by the penetrant remover which added the Nonion activator to rubbing alcohol 0.01%, MRSA was made to adhere similarly and the number of micro organisms after 24-hour progress (a cell/ml) was investigated.

O ... The number of micro organisms after 24-hour progress was less than [ of the early number of micro organisms ] 1/100.

\*\* ... The numbers of micro organisms after 24-hour progress were 1/100 or more [ of the early number of micro organisms ], and less than 1/10.

x ... The number of micro organisms after 24-hour progress was 1/ 0 or more [ of the early number of micro

organisms ].

[0034] (2) The difference (\*\*E) of the color of film one year immediately after paint and after paint and the color of a standard board was measured using the discoloration color difference meter (SM color computer, product made from SUGA Testing machine).

O ... \*\*E≤2x ... \*\*E>2. [0035] (3) The state of the paint film of the bending part when bending at 180 degrees of bending nature was observed.

O ... Exfoliation-less x ... Those with exfoliation. [0036] (4) Corrosion resistance JIS Based on K5400.9, slitting was put in so that the upper shell metal plate of a paint film might be reached, and it held in salt spray test equipment for 2000 hours, and bulging and rust of a paint film by the salt water from the slitting section were observed.

O ... Bulging and rust-less x ... Bulging and those with rust. [0037] (5) Storage stability JIS of a paint The stability of a paint was observed after saving for six months at 40 degrees C based on K5400.4.

O ... It is [ no hard lump etc. ] and was uniform.

x ... It is [ a hard lump etc. ] and was not uniform.

[0038]

Table [ ] 5 . Evaluation criteria Example 1 Example 2 Example 3 Antibacterial Immediately after paint O O O One year after paint O O O One year after paint, after washing O O O Discoloration Immediately after paint O O O One year after paint O O O bending nature OO O corrosion resistance O O O Storage stability OO O [0039]

Table 5 (continuation) Evaluation criteria Example 1 of comparison Example 2 of comparison. Example 3 of comparison Example 4 of comparison Antibacterial Immediately after paint \* \* \* \* \* One year after paint x \* \* \* \* \* One year after paint, after washing x \* \* \* \* \* Discoloration Immediately after paint O x O O One year after [ paint ] xx OO Bending nature xO O O corrosion resistance xO OO Storage stability Ox x x [0040] In any [ one year immediately after paint and after paint ] case, there is no discoloration of a paint film, and the antibacterial precoat metal plate of examples 1-3 is excellent in antibacterial, antibacterial [ after washing ], processability, and corrosion resistance so that clearly from Table 5. On the other hand, in any [ one year immediately after paint and after paint ] case, the paint board of the example 1 of comparison and the precoat metal plate of the examples 2-4 of comparison are inferior to antibacterial.

[0041]

[Effect of the Invention] Since the antibacterial precoat metal plate of this invention has a coat more than two-layer and the antimicrobial agent which consists of a zeolite system support with a particle size of 0.05-5 micrometers which it is [ support ] the antibacterial precoat metal plate whose best layer is a clear layer, and made the complex ion support in the baking coat of the aforementioned clear layer is contained 0.1 to 5% of the weight on solid-content criteria, it excels in antibacterial and the processability after baking finish, and even if it uses it for a long period of time, there is no discoloration of a paint film, and antibacterial

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[Translation done.]